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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-90-J-1148

R & T Code 4132016



*Design, Synthesis and Characterization
of Novel Nonlinear Optical Polymers*

Dr. Sukant Tripathy
University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, Massachusetts 01854

94-22725

310 May 31, 1994



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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R & T : 4132016

GRANT Number: N00014-90-J-1148

GRANT Title: **Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers**

Principal Investigator: Dr. Sukant Tripathy

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Part I

- a. Number of papers submitted to refereed journals, but not published: 6
- b. Number of papers published in refereed journals (list attached): 11
- c. Number of books or chapters submitted, but not yet published: 1
- d. Number of books or chapters published (list attached): 0
- e. Number of printed technical reports & non-refereed papers (list attached): 6
- f. Number of patents filed(pending): 5
- g. Number of patents granted (list attached): 4
- h. Number of invited presentations (list attached): 8
- i. Number of submitted presentations(list attached): 8
- j. Honors/Awards/Prizes for contract/grant employees (list attached): 5

- k. Total number of full-time equivalent graduate students and post-doctoral associates supported during this period, under this R & T project number:

Graduate Students: **2**

Post-Doctoral Associates: **1**

including the number of,

Female Graduate Students: **1**

Female Post-Doctoral Associates: **0**

the number of,

Minority Graduate Students: **0**

Minority Post-Doctoral Associates: **0**

and the number of,

Asian Graduate Students: **1**

Asian Post-Doctoral Associates: **1**

- l. Other funding (list agency, grant title, amount received this year, total amount, and the period of performance, and briefly state the relationship of that research to your ONR grant):

The Petroleum Research Foundation funding is ending in August 1994.

The URI grant from Army Research Office(Ken Marx PI) has ended and has been provided with a small extension.

The Spire funding is for technology development and is mostly expended.

Funding from Natick is for a joint project with Dave Tirell from UMass Amherst that ends in October 1994.

Department of the Army, University Research Initiative, "*Intelligent Materials and Structures Based on Ordered Assemblies of DNA*" co-principal investigator with Professors Kenneth Marx and Jayant Kumar, Research Grant, March 15, 1993 - February 15, 1995 - \$69,282.00.

American Chemical Society/Petroleum Research Fund, "*Novel Photocrosslinked NLO Polymers and Related Electro-Optic Device*" Research Grant, January 1, 1992 - August 31, 1994 - \$43,000.00

Spire Corporation, "*Polymeric Materials for Second Harmonic Generations*" Research Grant, August 11, 1993 - April 15, 1995 - \$60,000.00.

National Science Foundation, "*Interpenetrating Network Second Order Nonlinear optical Polymers*" Research Grant, March 1, 1994 - February 28, 1997, \$80,000.00.

U.S. Army, Natick, "*Engineering of Proteins and Devices for Biosensor Applications*", Research Grant, April 1, 1993 - September 30, 1994, \$47,495.00.

Part II

- a. Principal Investigator: Dr. Sukant Tripathy
- b. Current telephone number: 508-458-7116
- c. Cognizant Scientific Officer: Dr. JoAnn Milliken
- d. Brief description of the project.

The principal focus of the project is to develop new materials chemistry based on molecular level design and solid state chemistry. The goals have been to develop electroactive polymers with novel electronic, optical and nonlinear optical properties. Second and third order nonlinear optical materials have been developed based on conjugated macromolecules and asymmetric anharmonic molecular electronic dipolar oscillators.

In this multidisciplinary research effort, starting from the first principle, polymeric systems have been developed with stable large nonlinear optical coefficients, ultrathin electroactive redox monolayers, molecular superlattices, and others. Sol-gel chemistry, photochemical crosslinking and photopolymerization have been employed as engineering tools in materials fabrication and to elicit new phenomenon.

Bulk self assembly processing techniques needed to control the molecular and supermolecular organizations of optical and electroactive molecules have also been developed. They include spontaneous molecular organization of nonlinear optically active conjugated polymers such as polydiacetylenes with conjugating and hydrogen bonding side groups.

- e. Significant results during last year.

The relaxation behavior of NLO chromophores in the IPNs is fundamentally different from that of guest/host systems. Crosslinked NLO-active networks exhibit superb stability compared to guest/host and side-chain systems even when the temperature is close to T_g of the polymers.

A new class of all organic sol-gel materials for second-order nonlinear optical applications has been prepared for the first time.

A new macro molecular self-assembly concept and process has been developed based on an asymmetrically substituted soluble

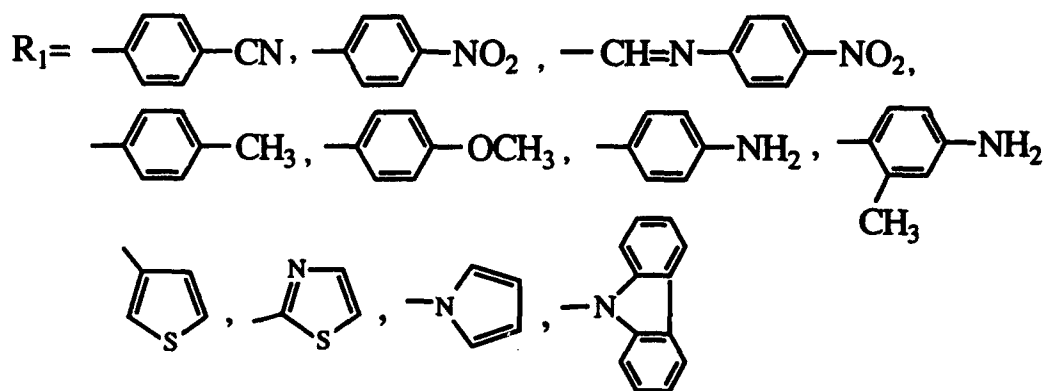
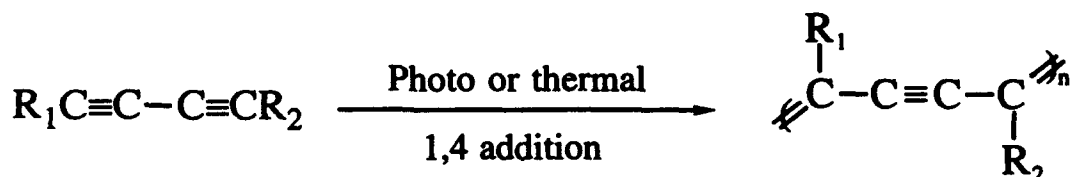
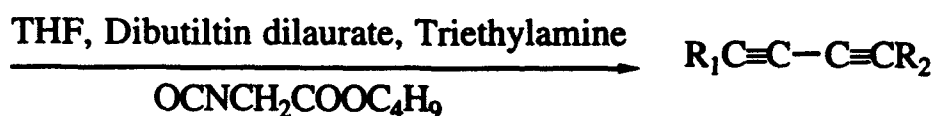
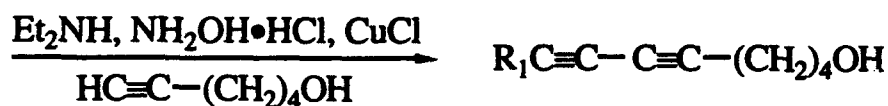
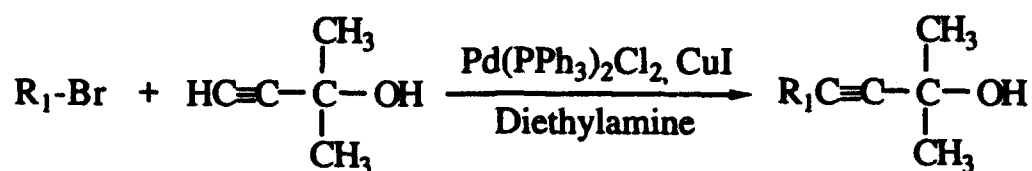
polydiacetylenes, poly(BPOD). The idea is to employ an NLO active chromophore (R1) as one of the substituents and a flexible, hydrogen bond forming moiety (R2) as the second substituent.

f. Brief summary of plans for next years work

Molecular Systems Design and Synthesis: A new bulk self assembly processing technique needed to control the molecular and supermolecular organizations of NLO active conjugated polymers such as polydiacetylenes, polythiophenes and poly(1,4-phenylene vinylene) derivatives will be investigated. The idea is to employ an NLO active chromophore as one of the substituents and a flexible, hydrogen bond forming moiety as the second substituent. The polar, flexible groups not only help to form a stable self organization by means of intramolecular hydrogen bonds, they are also known to promote solubilization of the polymer. Since we are utilizing a conjugated polymer backbone, high degree of third order NLO activity is also expected. Synthetic schemes of the various polydiacetylenes, poly(1,4-phenylene vinylene) derivatives, and polythiophenes of interest are described in Schemes 1-3, respectively.

Processing and fabrication: No special technique or substrate is necessary for fabrication of these soluble conjugated polymers. Upon spin coating or casting from solutions, the polymer chains self organize in an acentric stable polar organization without recourse to poling. The acentric self alignment necessary for the second order NLO properties is mainly due to the combined effect of asymmetry of the two side groups and the spontaneous alignment of the polar, flexible moiety with the aid of intramolecular hydrogen bonding.

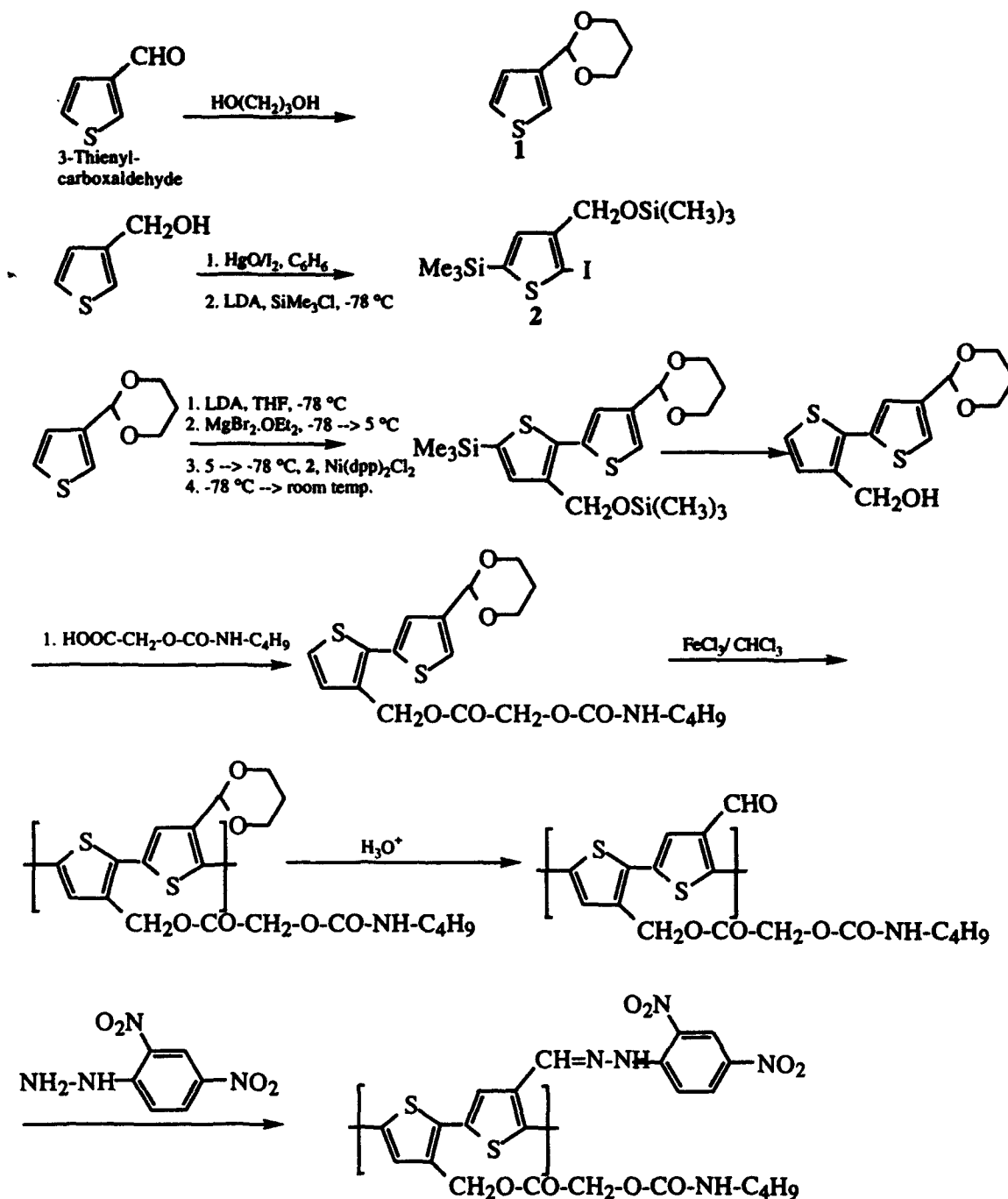
Characterization: Numerous solid state characterization techniques are being employed. Polarized FT-IR, FT-Raman, and UV-Vis-NIR spectroscopies will be utilized to investigate the alignment of the side groups of the polymer films. Other linear and nonlinear optical properties will be investigated. Dynamic mechanical analysis, dielectric measurements and thermal analysis will be carried out to study the molecular motion organization and property aspect. Photoconductivity and photovoltage will be measured. Electron microscopy study will be carried out to monitor the changes occurring in the crystal lattice during polymerization and to investigate the morphology. Second and third harmonic generation are other properties of interest.



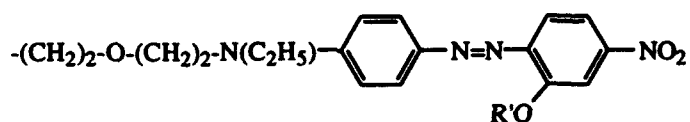
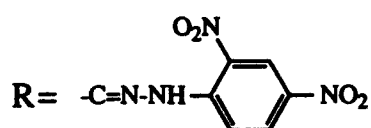
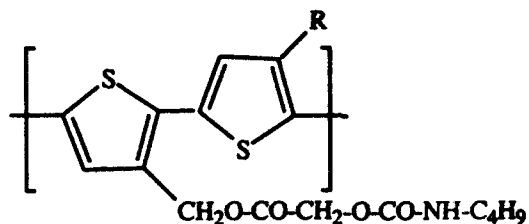
Scheme 1. Synthetic route to various polydiacetylenes proposed as new Self Assembled Bulk(SAB) electro-optical materials.



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Scheme 3-A. Proposed route for the synthesis of asymmetrically substituted polythiophene derivatives proposed as new electro-optical materials.



Where R' = C₆H₅-CH=CH-CO-
CH₂=C(CH₃)-CO-

Scheme 3-B. Various polythiophene derivatives proposed as new electro-optical materials. Continues from previous page.

- g. Name of graduate students and post-doctorals currently working on the project.

Post-doctoral

Dr. Woo Hong Kim.

Graduate students (Ph.D. Candidates)

Mr. Govindasamy Chittibabu

Mr. Dong Yu Kim

Department

Chemistry

Chemistry

Undergraduate students

Mr. Craig E. Masse

Mr. John Patronick

Department

Chemistry

Chemistry

Part III

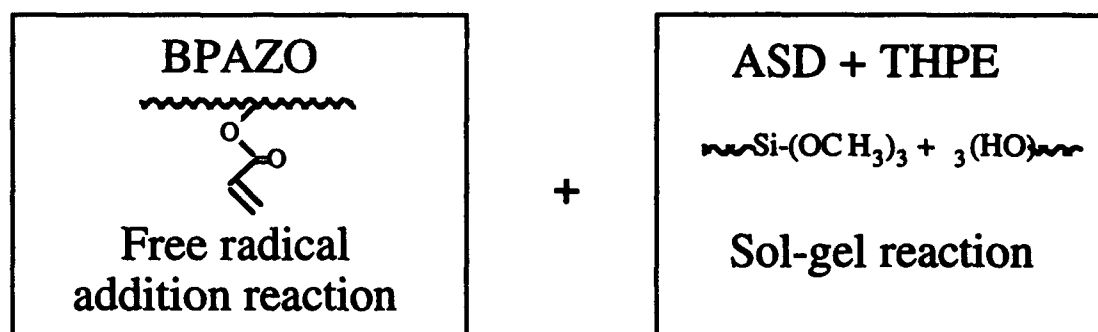
Research Highlights

Goal:

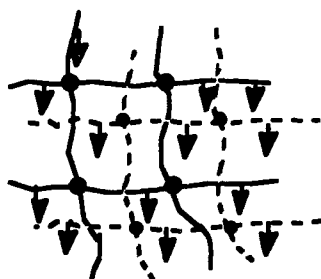
- * To investigate and understand the relaxation behavior of ordered nonlinear optical (NLO) chromophores in a highly crosslinked polymer matrix.

Approach:

- * An interpenetrating polymer network incorporating NLO active chromophores is prepared.
- * The decay of second harmonic generation (SHG) intensity at various temperatures was monitored.
- * The relaxation behaviors of NLO chromophores in the IPN and guest/host systems are directly compared.

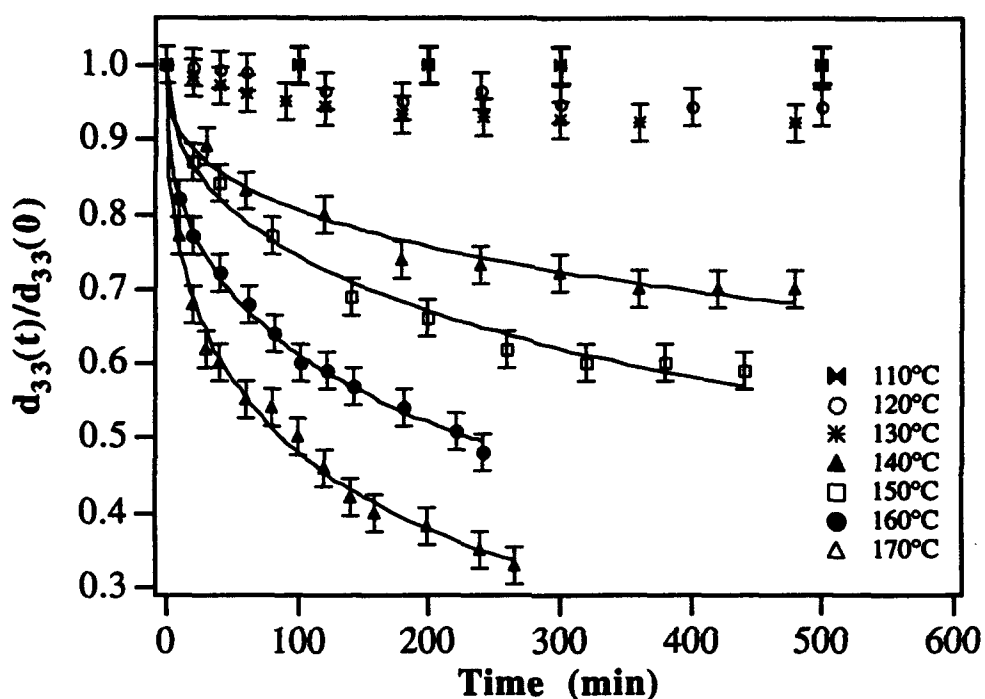


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\downarrow NLO active chromophores

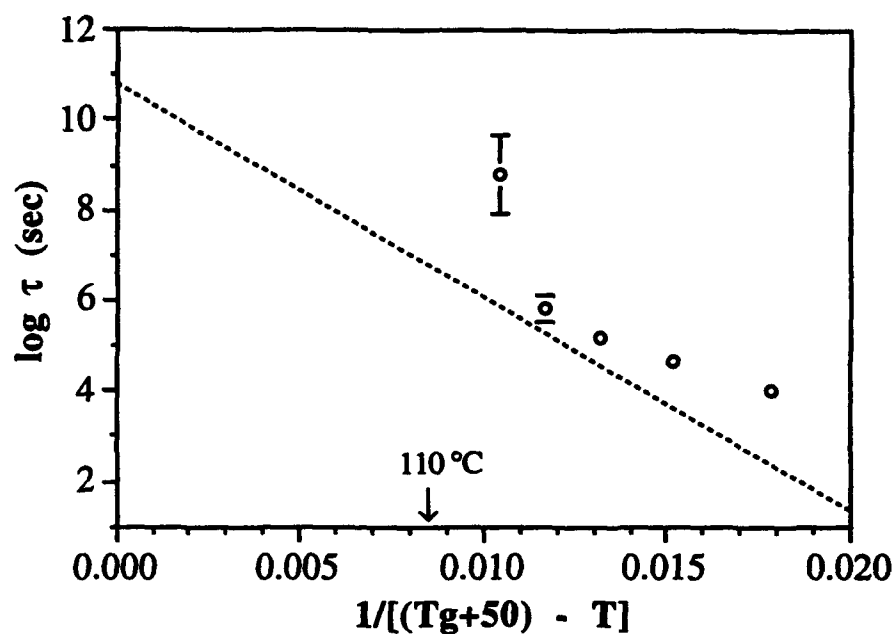
Schematic diagram for the formation of the IPN.



Temporal behavior of the second harmonic coefficient of the IPN at different temperatures.

Kohlrausch-Williams-Watts equation was used to characterize the relaxation time t .

$$d_{\text{eff}}(t)/d_{\text{eff}}(0) = \exp[-(t/t)^b], \quad 0 < b < 1$$



Relaxation time t as a function of $1/(T_g+50 - T)$ for the IPN samples at 130, 140, 150, 160, and 170 °C. The dashed line is the master curve that is expected to fit guest/host systems.

Summary:

- * The relaxation behavior of NLO chromophores in the PN is fundamentally different from that of guest/host systems.
- * The results support that crosslinked networks in NLO polymeric systems play an important role in enhancing the stability of the NLO properties.

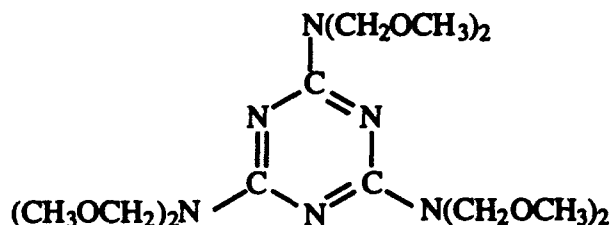
Goal:

- * To design and synthesize all organic sol-gel materials exhibiting second-order NLO properties and low optical loss for photonic applications.

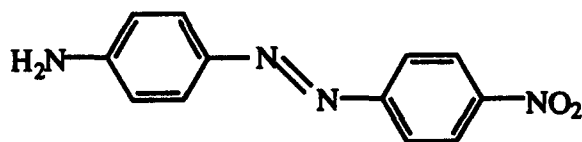
Approach:

- * Hexa(methoxymethyl)melamine (HMM) prepolymer doped with Disperse Orange 3 (DO3) was investigated.
- * NLO dye and HMM prepolymer were dissolved in organic solvent with a certain amount of water and acid catalyst. The solution was heated at 150 °C for 1 h before spin-coating.
- * Corona poling technique was used to obtain the second-order NLO property in the polymer films. Poling/curing condition was chosen to be 220 °C for 30 min.

(a) HMM



(b) DO3



Chemical Structures of (a) HMM and (b) DO3

- * Second-order NLO coeff., $d_{33} = 10.7$ pm/V.
- * d_{33} value showed a slow decay at 100°C .
- * Polymer waveguide optical loss was determined to be 3.7 dB/cm at 833 nm.

Summary:

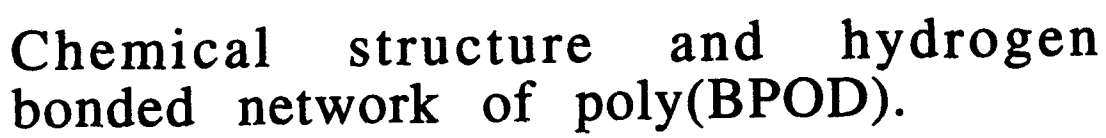
- * A new class of all organic sol-gel melamine based polymeric materials for second-order nonlinear optics has been demonstrated for the first time.
- * The materials possess low optical loss. Properties can be further enhanced by optimization of compositions and processing conditions.
- * These polymers are good candidates for the fabrication of optical waveguide devices.

Goal:

- * To develop bulk self assembled conjugated polymers as second and third order nonlinear optical (NLO) materials.

Approach:

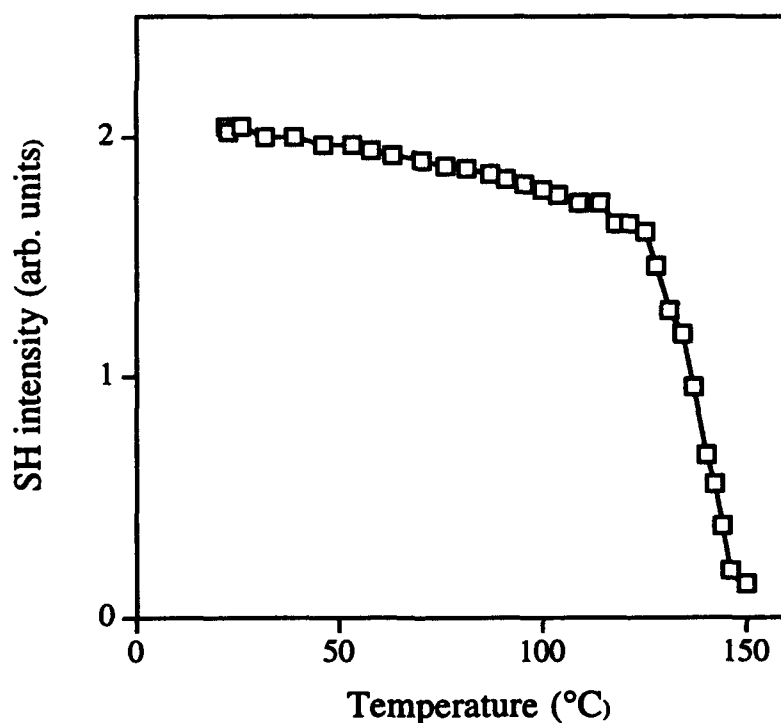
- * Conjugated polymers such as asymmetrically substituted polydiacetylenes are utilized as novel second and third order NLO materials.
- * NLO active chromophore is attached as one of the substituents to improve the nonlinearity and a hydrogen bond forming polar, flexible moiety is employed to promote self organization and improve solubility.



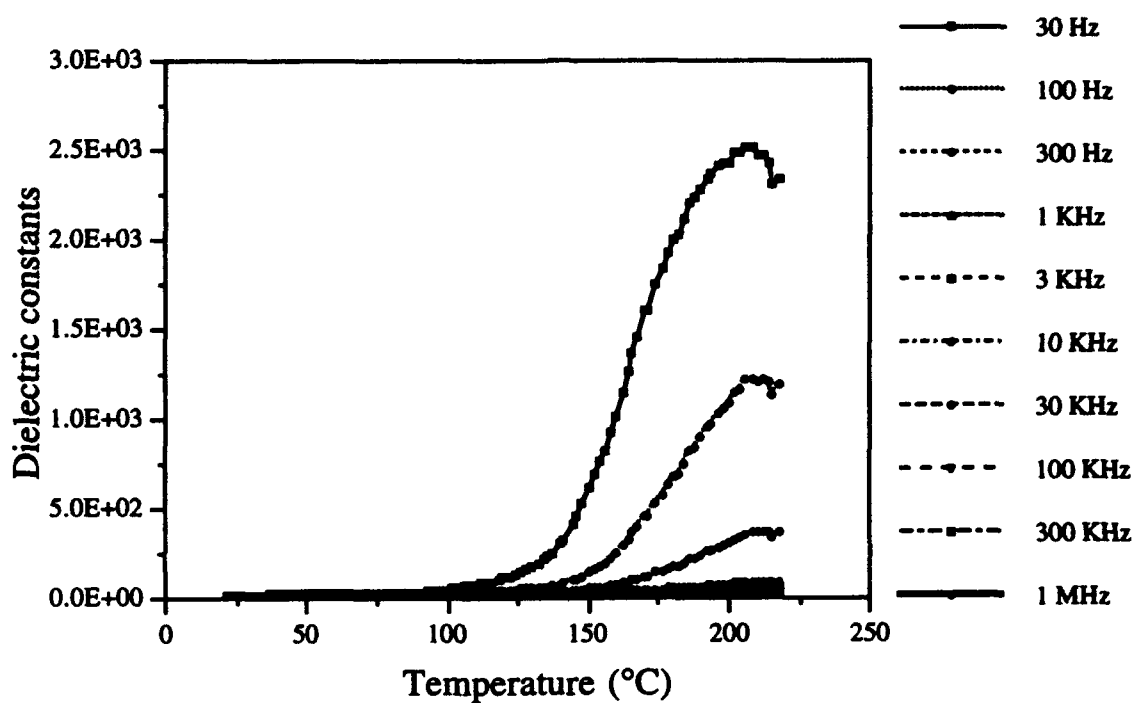
Chemical structure and hydrogen bonded network of poly(BPOD).

d_{33} values for poly(BPOD) spin coated films at incident wavelength of 1.06 μm .

Film thickness (μm)	d_{33} (pm/V)	
	w/o abs. correction	with abs. correction
0.31	0.74	5.57
0.25	0.78	4.43
0.19	0.88	3.32



Plot of second harmonic intensity from spin coated film of poly(BPOD) at various temperatures.



Temperature dependence of dielectric constants of spin coated film of poly(BPOD) at various frequencies.

Summary:

- * Polymer chains of a novel asymmetric polydiacetylene, BPOD, self assemble in an acentric stable polar organization upon spin coating. Spontaneous alignment of the urethane moiety aided by the intramolecular hydrogen bonds between the side groups appear to be responsible for this organization.
- * The invention of this self assembling second order NLO polymer opens up numerous possibilities in molecular design for further optimization of properties.

Attachment page 1

b. Number of papers published in refereed journals (list attached): 11

1. "Dipolar Relaxation in a Second-Order Nonlinear Optical Interpenetrating Polymer Network", J.-I. Chen, S. Marturunkakul, L. Li, R. J. Jeng, J. Kumar, and S. K. Tripathy *Macromolecules* **26**, 7379 (1993)
2. "Relaxation Behavior of a Nonlinear Optical Polyimide/Inorganic Composite", S. Marturunkakul, J.-I. Chen, R. J. Jeng, S. Sengupta, J. Kumar, and S. K. Tripathy *Chem. Mater.* **5**, 743.(1993).
3. "A Novel, Soluble Poly(Diacetylene) Containing An Aromatic Substituent", W.H. Kim, N.B. Kodalil, J. Kumar, S.K. Tripathy, *Macromolecules*, **27**, pp. 1819-1824, 1994.
4. "Second Order Nonlinear Optical Properties of a Polymer Exhibiting Optical Transparency Down to 340 nm", M. Kamath, C.E. Masse, R.J. Jeng, M. Cazeca, J. Kumar, S.K. Tripathy, *J. Macromol. Sci., Pure and Applied Chem.*, A31 (1994).
5. "Novel Polydiacetylenes with Chromophoric Substituents: Materials for Second and Third Order Nonlinear Optics", C.E. Masse, W.H. Kim, B. Bihari, S.K. Tripathy, J. Kumar, *Molecular Crystals Liquid Crystals* , February 1994.
6. "Synthesis and Properties of a Novel Polythiophene Derivative with a Side-Chain NLO Chromophore", K. G. Chittibabu, L. Li, M. Kamath, J. Kumar, S. K. Tripathy, *Chem Mater.*, **6**, 475-480, 1994.
7. "Conformational Polymorphism of Di(2-naphthyl) Ditelluride", D.J. Sandman, L. Li, and S.K. Tripathy, *Organometallics* **13** 348 (1994).
8. "Cerenkov Type Phase-Matched Second Harmonic Generation in Polymeric Channel Waveguides", Y. Chen, M. Kamath, A. Jain, J. Kumar and S. Tripathy, *Optics Communications* **101** 231 (1993).
9. "Molecular Dynamics Simulation of Substituted Conjugated Ionic Polyacetylenes" X.F. Sun, S.B. Clough, S. Subramanyam, A. Blumstein and S.K. Tripathy *Macromolecules* **26** 597 (1993).
10. "Novel Organic Sol-Gel Materials for Second-Order Nonlinear Optics", R. J. Jeng, G. H. Hsiue, J.-I. Chen, S. Marturunkakul, L. Li, X. L. Jiang, C. Masse, J. Kumar, and S. K. Tripathy, *Electrical*,

Attachment page 2

Optical and Magnetic Properties of Organic Solid State Materials, A.F. Garito, A. K-Y Jen, L.R. Dalton, and C. Y-C Lee, Eds.; MRS Sym. Proc. Vol. 328; Material Research Society: Pittsburgh, pp 583-588.

11. "Polyimide/Inorganic Composite-Interpenetrating Polymer Network for Stable Second-Order Nonlinear Optics", S. Marturunkakul, J.-I. Chen, L. Li, X. L. Jiang, R. J. Jeng, J. Kumar, and S. K. Tripathy In *Electrical, Optical and Magnetic Properties of Organic Solid State Materials*, A. F. Garito, A. K-Y Jen, L. R. Dalton, and C. Y-C Lee, Eds.; MRS Sym. Proc. Vol. 328; Material Research Society: Pittsburgh, pp 541-546.

d. Number of books or chapters published 0

e. Number of non-referred papers (list attached): 6

1. "Interpenetrating Polymer Networks with Stable Second-Order Optical Nonlinearity via an *In Situ* Sol-Gel Reaction", J.-I. Chen, S. Marturunkakul, L. Li, R. J. Jeng, J. Kumar, and S. K. Tripathy In *Organic Thin Films for Photonic Applications Technical Digest, 1993*; Optical Society of America: Washington, D.C., 1993, Vol. 17, pp. 282-285.
2. "Design, Synthesis, and Characterization of a New Class of Second Order Nonlinear Optical Organic/Inorganic Composites", R. J. Jeng, J.-I. Chen, S. Marturunkakul, Y. M. Chen, J. Kumar, and S. K. Tripathy, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1993, 34(2), 777.
3. "Stable Second-Order Nonlinear Optical Materials Based On Interpenetrating Polymer Networks", S. Marturunkakul, J.-I. Chen, L. Li, X. L. Jiang, R. J. Jeng, S. K. Sengupta, J. Kumar, and S. K. Tripathy, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1994, 35(2).
4. "Novel Polydiacetylenes with Chromophoric Substituents" C.E. Masse, N.B. Kodali, L. Li, J. Kumar, and S.K. Tripathy. *Polym. Prepr., Am. Chem. Soc.*, 1, 724 (1993).
5. "Stable Second-Order Nonlinear Optical Materials Based on Interpenetrating Polymer Networks", S. Marturunkakul, J.-I. Chen,

Attachment page 3

L. Li, X.L. Jiang, R.J. Jeng, S.K. Sengupta, J. Kumar, and S.K. Tripathy, submitted to *ACS Fall Meeting* (1994).

6. "Second-Order Nonlinear Optical Polymers: from Fundamentals to Applications", S. Marturunkakul, J.-I. Chen, L. Li, M. Cazeca, S. Sengupta, S. Tripathy, J. Kumar, X.L. Jiang, R.J. Jeng, submitted to *ACS Spring Meeting* (1994).

g. Number of Patents granted (list attached): 4

1. "Photocrosslinked Second Order Nonlinear Optical Polymers", (B.K. Mandal J. Kumar, J.C. Huang) Granted Patent No.5,112,881 Assignment (UOL 90-05).
2. "Thermostable Second Harmonic Generating Photocrosslinkable Polymers" (B.K. Mandal and J. Kumar) Granted reel 5337, frames 568, 569 & 570 Assignment (UOL 90-09).
3. "Photocrosslinked Second Order Nonlinear Optical Polymers", (J. Kumar, S. K. Tripathy, B. Mandal, J. C. Huang) Granted, Patent No. 5,223,356 Assignment (UOL 90-09A and 90-05A).
4. "Photocrosslinked Second Order Nonlinear Optical Polymers", (B. Mandal, S. Tripathy, J. C. Huang, J. Kumar) Granted, Patent 5,290,824 Assignment (UOL 90-07X).

h. Number of invited presentations (list attached): 8

1. "Second-Order Nonlinear Optical Polymers: From Fundamentals To Applications", S. K. Tripathy, J. Kumar, X. L. Jiang, R. J. Jeng, S. Marturunkakul, J.-I. Chen, L. Li, M. Cazeca, and S. Sengupta, presented by S. Tripathy at ACS Spring Meeting, San Diego, CA, March, 1994.
2. "Nonlinear Optical Polymers Derived From Organic/Inorganic Composites" S. K. Tripathy, J. Kumar, J.-I. Chen, S. Marturunkakul, R. J. Jeng, L. Li, and X. L. Jiang, presented by S. Tripathy at the Symposium "Better Ceramics Through Chemistry" at the MRS Spring Meeting in San Francisco, April, 1994.

Attachment page 4

3. "Photocrosslinkable Conducting Polymers as Nonlinear Optical Materials", L. Li, K G. Chittibabu, J. Kumar, Sukant Tripathy, *SPIE Proceedings 2042* 1993. Conference on Photopolymers and Application in Holography, Optical Data Storage, Optical Sensors and Interconnects, SPIE, Quebec, 1993.
4. "Intriguing Supramolecular Assemblies with Electronically Conjugated Components", Sukant Tripathy, presented at the 206th ACS National Meeting, Chicago, IL, August, 1993.
5. "Stable Second Order Nonlinear Optic Polymers", Sukant Tripathy, presented at National Academy of Science, Washington, DC, November, 1993.
6. "Polymers for Photonics Applications", Sukant Tripathy, invited Seminar at Materials Technology for Competitive Advantage, St. Petersburg Beach, FL, November, 1993.
7. "New Developments in Second-Order Nonlinear Optical Polymeric Materials", S. K. Tripathy, W.H. Kim, B. Bihari, D.W. Cheong and J. Kumar, presented by S. K. Tripathy at Materials Research Society, Fall Meeting, Boston, MA. 1993.
8. "Sol-Gel Derived Second Order Nonlinear Optic Polymers", Sukant Tripathy, invited Seminar at National Research Laboratory, Washington, DC, December, 1993.

i. Number of Presentations (list attached): 8

1. "Novel Polydiacetylenes As Materials For Second And Third Order Nonlinear Optics", W. H. Kim, C. E. Masse, B. Bihari, J. Kumar. S. K. Tripathy, Materials Research Society, Fall 1993, Boston, MA.
2. "Novel Polydiacetylenes with Chromophoric Substituents" C.E. Masse, presented at the 205th National Meeting of the American Chemical Society, Denver, CO, March 1993.
3. "Novel Polydiacetylenes with Chromophoric Substituents: Materials for Second and Third Order Nonlinear Optics" C.E. Masse, presented at conference on "Optical Probes of Conjugated Polymers and Fullerenes", Salt Lake City, UT, February 1994.

Attachment page 5

4. "Diacetylenes for Second and Third Order Nonlinear Optics" C.E. Masse, to be presented at International IUPAC Symposium on Functional and High Performance Polymers in Taipei, Taiwan, November 14-16, 1994.
5. "Design, Synthesis, and Characterization of a New Class of Silicon Containing Second Order Nonlinear Optical Materials", R. J. Jeng, J.-I. Chen, S. Marturunkakul, Y. M. Chen, J. Kumar, and S. K. Tripathy, presented by J.-I. Chen at the 206th ACS National Meeting, Chicago, IL, August, 1993.
6. "An Interpenetrating Polymer Network As A Stable Second Order Nonlinear Optical Material: Comparison With The Guest/Host Systems", S. Marturunkakul, J. Kumar, and S. K. Tripathy, presented by S. Marturunkakul at the 206th ACS National Meeting, Chicago, IL, August, 1993.
7. "Polyimide/Inorganic Composite - Interpenetrating Polymer Network For Stable Second-Order Nonlinear Optics", S. Marturunkakul, J.-I. Chen, L. Li, X. L. Jiang, R. J. Jeng, J. Kumar, and S. K. Tripathy, presented by S. Marturunkakul at MRS Fall Meeting, Boston, MA, December, 1993.
8. "Novel Organic Sol-Gel Materials For Second-Order Nonlinear Optics", R. J. Jeng, G. H. Hsiue, J. I. Chen, S. Marturunkakul, L. Li, X. L. Jiang, C. Masse, J. Kumar, and S. K. Tripathy, presented by J.-I. Jeng at MRS Fall Meeting, Boston, MA, December, 1993.

j. Number of Honors/Awards/Prizes for contract/grant employees (list attached): 5

The Mark Jonathan Elliot outstanding graduate student award received by Mr. Woohong Kim, for his excellent academic performance, University of Massachusetts Lowell, May, 1994.

The American Chemical Society POLYED Division Award received by Mr. Craig E. Masse for his research on "Novel Diacetylene with a Chromophoric Substituents", March, 1994.

Attachment Page 6

The Cole Undergraduate Research Award, UMass-Lowell Sigma Xi Scientific Research Honor Society, received by Mr. Craig E. Masse for his research on "Novel Unsymmetrical Polydiacetylenes as Materials for Second and Third Order Nonlinear Optics" April, 1994.

The Graduate Student Professional Development Award received by Mr. Jeng-I Chen for presenting his research work at the 206th American Chemical Society National Meeting in Chicago, IL., August, 1993.

The Graduate Student Professional Development Award received by Ms. Sutiyo Marturunkakul , for presenting her research work at the 206th American Chemical Society National Meeting in Chicago, IL., August, 1993.